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Stifling magnesium corrosion via novel anodic coating

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Abstract

The use of light-weight magnesium (Mg) alloys as engineering materials has been hampered in part due to their poor corrosion performance. This work aims to address the corrosion issue of Mg by introducing a functional protective coating system consisting of an intermediate active metallic film (anodic with respect to Mg) and an outer passive coating to slow the rate of dissolution of the intermediate active metallic film; which is akin to the protective surface coating system utilized for galvanised steel. If the outer passive coating is damaged or loses its integrity, the active (i.e. anodic) coating is expected to electrochemically sacrifice itself to impose protection upon the underlying Mg substrate. This work represents a novel corrosion protection system for Mg, and is demonstrated herein for a lanthanum based coating system upon commercial Mg-alloy AZ91D.

Key words: Magnesium alloys, Corrosion, Anodic coating, Lanthanum, Conversion coating

Introduction

The use of surface coatings for the protection of reactive (non-passive) metals such as iron and steel, presents a practical solution to corrosion control. The variety of possible coatings applied to engineering alloys varies widely and may include simple paint, barrier coatings (epoxy, urethanes, etc.), conversion coatings, plating and metallic coatings, to sacrificial coatings [1, 2]. The latter, sacrificial coatings, present the archetypical functional coating.. To that end, sacrificial coatings perform active ‘cathodic protection’ by serving as a sacrificial anode, as demonstrated by galvanizing of iron and steel [3]. Steel possesses a corrosion potential in most neutral aqueous media of ~ -0.7 to -0.5 V_{SCE} , and is readily protected by Zn, Al or Mg (which have or possess potentials of ~ -1.0 to 1.2 V_{SCE} , -0.8 to -1.1 V_{SCE} , and ~ -1.6 V_{SCE} respectively) in similar electrolytes [2].

With respect to corrosion of magnesium (Mg), the inherently high rates of Mg and Mg-alloy corrosion in aqueous media present a significant issue to wider use of Mg [4, 5]. Of the so-called engineering or structural metals, Mg has the highest corrosion rates (by a large margin) and control of Mg-alloy corrosion either requires appropriate alloying, or surface coatings [6, 7]. Alloying for corrosion resistance is not feasible in many cases, as this would restrict use to a finite number of alloys that may not have the requisite mechanical properties. As such, essentially all Mg-alloys are coated by some means prior to service. The most common coatings principally include: (i) chemical conversion coatings for the purposes of transforming the alloy surface to a less soluble compound (such as a metal phosphate) [7], (ii) barrier coatings which provide a physical barrier to the environment (such as polymeric systems) [8], or (iii) inert metals such as Ni-plating [9-11].

However, the major issue with the coating technologies (i) to (iii), is that they can only protect the underlying Mg when they are pristine and in-tact. In other words, any coating defect renders the localised portion of exposed Mg as an intense local anode, allow corrosion

to proceed at what is often alarmingly high rates. As such, conversion and barrier films perform satisfactorily as long as their integrity can be maintained. This feature is a limitation to the present corrosion protection technology for Mg.

Following the principles of sacrificial coatings such as galvanising of steel, one solution to corrosion protection of Mg is to employ a sacrificial coating. Barrier coatings do not function to protect defect sites where the underlying alloy is exposed. Hence functional ability to protect scratches either via cathodic protection or prevention and/or inhibitor release are high desired attributes in coatings. The rationale is that the even in the presence of a defect or damage, sacrificial (i.e. anodic) coatings are functional on the basis that they protect any exposed underlying metal. To this end, the only report to date for such sacrificial protection of Mg-alloys was reported by Yu and Uan [12], whereby pure Mg was deposited as sacrificial anode upon Mg alloy AZ91D. The potential difference between Mg and AZ91D was ~210 mV – however the protective performance was not satisfactory, which is likely attributed to the minimisation of potential difference with time owing to so-called ‘cathodic activation’ of Mg which is accompanied by an increase in potential with dissolution [13]. The development of sacrificial coatings for Mg has not been well chartered to date, and indeed given the electronegativity of Mg, this remains a challenge. Viable options for metals that are anodic (i.e. more electroactive) to Mg and Mg-alloys are quite limited. Candidates include the entire series of alkali metals (Li, Na, K, Rb), perhaps some alkaline earth metals (i.e. Ca) and some of the rare earth elements (i.e. La, Eu, Gd, etc.) [14]. Whilst the list of viable elements is not exhaustive, it is clear that the elements listed are very reactive, and most are untenable on the basis of being unstable in air. Of the viable candidates, it was recently reported that rare earth metals (which are comparatively cheap and air stable), present corrosion potentials in aqueous electrolytes that are more negative than that of Mg [14]. A standout rare earth metal was lanthanum (La), which was shown to maintain corrosion

potentials more negative than Mg and Mg-alloys over a range of electrolyte conditions [14].

Rare earth metals are capable of being deposited using various known methods, such as hot dipping (in controlled environments), electroplating, or plasma sputtering [8]. The plasma sputtering (plasma vapour deposition) process is a simple method to yield quality thin metal films [15-17] and was thus used in this study as ready the means to generate an anodic La coating upon an Mg-alloy (AZ91D) substrate. To date, there have been no reports regarding anodic coatings comprised of rare earth metals upon Mg-alloys.

As expected, a sacrificial La coating would be consumed very rapidly due to the high reactivity of La, and the fact that the La would be anodically polarised when at a mixed potential in contact with Mg. As such, in this work, in order to prolong the lifespan of the produced La coating, a means to kinetically restrict dissolution of the sacrificial La coating is of importance. Such a concept is actually not foreign on the basis that even Zn coatings upon steel are protected by coating the sacrificial Zn in order to kinetically restrict its dissolution and prolong the coating lifetime. In order to kinetically restrict the dissolution of La, a passive conversion coating would be one approach for achieving this. A conversion coating is a simple coating that forms by immersion of a metal in an ion rich electrolyte that reacts with a metal surface to generate a metal ion concentration and pH difference at the metal-electrolyte interface. This then facilitates precipitation from the solution onto the substrate, forming a surface coating. Whilst pre-empting the results herein, we note that a practical challenge faced is that although substantial efforts have focused on investigating conversion coatings for various metals [18-21], essentially no work has been performed to date regarding conversion coating upon La. Since the anodic coating layer being investigated herein is La, a suitable conversion coating for La is of importance.

Using equilibrium thermodynamics calculations to explore possible conversion coatings (which is nowadays increasingly common [22]) for La, it was determined that La-phosphate

(LaPO₄) is an insoluble compound over a wide range of pH and potentials. The results of such calculations are shown in Figure 1, where it can be seen that the compound LaPO₄ is stable within the entire pH range for pH >6; and this is reconciled with the solubility of LaPO₄ being low. Consequently, LaPO₄ was defined as a suitable candidate in terms of restricting the dissolution of La. With such a notion in mind, the design of the protective coating system for Mg-alloys herein is depicted in Figure 2, whereby La is applied onto the Mg substrate (going from Fig. 2A to 2B), with some of the La film subsequently consumed to generate a LaPO₄ conversion coating as an outer layer (Fig. 2C). For such a functional coating system, when coating integrity is good, LaPO₄ can provide sufficient protection; however when the conversion coating layer is damaged to penetrate the Mg-substrate, the anodic La film will electrochemically sacrifice itself to protect the underlying Mg-substrate. These concepts, and their practical demonstration, are reported herein, with ramifications for a novel protection system capable of offering corrosion protection to Mg and its alloys.

2. Experimental

2.1 Materials and deposition

Mg alloy AZ91D produced by high-pressure die-casting (at CSIRO Australia) was studied. The composition (in wt.%) of the alloy was quantified using inductively coupled plasma-atomic emission spectroscopy, ICP-AES (Spectrometer services, Coburg, Australia) and is Mg-9.1Al-0.66Zn-0.24Mn. Specimens, of $\sim 15 \times 10 \times 3 \text{ mm}^3$ were prepared from the as casted alloy, were ground to 2000 grit SiC finish and ultrasonically cleaned in ethanol. Lanthanum (La) thin films were deposited upon the specimens by radio frequency (RF) magnetron sputtering (Hummer BC-20 DC/RF Sputter system, Anatech, USA). A high purity (99.5 %) La target (Ezzi Vision, Australia) was utilised for depositing La thin film. To ensure high quality deposits, the target was stored in a mineral oil, cleaned with petroleum ester (Sigma-Aldrich, Australia) and dried in air prior to each deposition. Further, the sputtering chamber was evacuated to 3.0×10^{-7} Torr and argon (Ar) gas (99.99% pure) was passed into the chamber. The deposition was carried out at 1.0×10^{-2} Torr at an applied 200 W RF power. The distance between the substrate (alloy specimens) and La target was fixed at 12 cm and the temperature of the substrate was maintained at 17°C. To minimise thermal stresses in the deposits, a total sputtering time of 2.5 h was divided in to a few short time periods with each period consisted of 40 min sputtering and a 10 min forced break.

In parallel to the deposition of La upon AZ91D Mg-alloy specimens, studies were also carried out on a pure bulk La specimen to assess the viability and performance of a passivating conversion coating upon a La specimen. The bulk La specimen (99.9% Alfa Aesar) was ground to 2000 grit SiC finish and ultrasonically cleaned in ethanol, prior to a conversion coating. The conversion coating was carried out in a bath containing 0.1M $\text{NH}_4\text{H}_2\text{PO}_4$ - to generate a lanthanum phosphate (LaPO_4) passive coating. The conversion coating bath was maintained at a constant temperature of 80°C. The coating/bath immersion

time was varied as reported in results section.

2.2 Microstructural characterisation

The surface topography and cross-section of a La deposited AZ91D alloy was studied using an FEI Helios NanoLab 600 focused ion beam – field emission scanning electron microscope (FIB-SEM). Prior to milling the La deposited specimen along its cross-section, a platinum (Pt) layer was deposited over the surface of La film to protect the film from ion beam damage. The specimens were then milled along the cross-section with a focused gallium (Ga^+) ion beam at an accelerating voltage of 30 kV and a current of 2.8 nA. Scanning electron micrographs were taken at a low accelerating voltage of 5 kV and 86 pA probe current.

2.3 Electrochemical characterisation

Potentiodynamic polarisation tests were carried out using a flat-cell (PAR, K0235, Princeton Applied Research, USA) containing 300 mL of 0.1M NaCl, and incorporating a saturated calomel (SCE) reference electrode, a platinum (Pt)-mesh counter electrode and with an exposed working electrode area of 1 cm^2 . The tests were performed at a sweep rate of 1 mV/s using a potentiostat/galvanostat (BioLogic® VMP-3Z) operated with an EC-Lab 10.32 software. Each test was carried out at least 5 times to ensure reproducibility.

The corrosion behaviour of both as deposited La films on the Mg-alloy specimens and conversion coated bulk La specimens were studied by immersing these specimens in 0.1 M NaCl solution and monitored in-situ using a mini hand-held digital microscope (CELESTRON, Australia).

3. Results and Discussion

3.1 Lanthanum coatings upon AZ91D via magnetron sputtering

Dense La films were capable of being successfully deposited upon Mg AZ91D alloys through magnetron sputtering. Uniform films were obtained by rotating the alloy specimens at a constant speed (of 4rad/s) during sputtering, thereby equally exposing the specimen surface. The deposited La-films were granular in their structure, such granular features being sub-micron sizes and with a uniform size distribution (Fig. 3A and 3B).

Using cross sectional microscopy as aided by FIB milling (Fig. 3C), the approximate film thickness was found to be $\sim 2.955\text{ }\mu\text{m}$, when La was sputtered for 2.5 h. The cross-section of the deposited specimen (Fig. 3C) shows three distinct layers; the uppermost layer is the protective platinum (Pt) film (in-situ deposited prior to FIB milling as a protective hard cap), the intermediate layer is the sputtered La film, and the bottom layer is the Mg substrate. The interface of La film and the AZ91D substrate is shown in Fig 3D. What is observed is that what appear to be nano-sized pores can be observed at the interface, however the interface is generally smooth and defect free. The pores observed are attributed to arising as a result of the surface roughness of the substrate prior to deposition.

3.2 Immersion testing of the deposited La films upon AZ91D

The sacrificial protection behaviour of the deposited La film upon Mg AZ91D alloys was examined by simple immersion testing. In order to generate a powerful visual analysis, protective tape was applied to a portion of the Mg-alloy substrate for a number of specimens prior to the La deposition. This tape allowed for a portion of the substrate to be masked, allowing for the production of specimen surfaces containing both uncoated and La-deposited regions. Such partially coated AZ91D specimens were subsequently immersed in 0.1 M NaCl solution to examine the evolution of their corrosion response. The corrosion response

occurring at progressive time intervals were imaged, and seen in Fig. 4.

What can be observed from Fig. 4 is that the initial colour of the La-film is rather dull. This appearance actually occurs rather spontaneously when the La-films are exposed to atmospheric air for a short time. Such surface darkening is synonymous with the non-lustrous appearance of rare earth metals. Following some exposure to 0.1 M NaCl solution, it is readily observed that the La-film was electrochemically consumed, sacrificially, while both the underlying Mg surface and the uncoated Mg surfaces remained pristine. Such observations are powerful, and validate the hypothesis that La will be sacrificial when coupled with Mg; which is due to the formation of a galvanic cell rendering the sputtered La-film as the anode, and the Mg-alloy (AZ91D) substrate as the cathode. As such, the magnetron sputtered La-layer is a functional protective layer when applied to Mg-alloys, however it is also obvious that its functional lifetime is short (in the range of tens of minutes).

3.3 Performance of conversion coated bulk lanthanum

In an attempt to prolong the lifetime and longevity of sacrificial La-films, conversion coating of La was pursued. To this end, bulk La (i.e. pure La ingot) specimens were utilised for ease of handling. The variation in conversion coating time was analysed as a variable by measuring the attendant polarisation response, as compared to untreated bulk La specimens. All the La samples conversion coated to achieve a LaPO_4 surface film displayed considerably reduced anodic dissolution kinetics as compared to the untreated La samples, as shown in Fig 5. In fact, the anodic dissolution of La was hindered by the conversion coating formed by exposure to 0.1M $\text{NH}_4\text{H}_2\text{PO}_4$ whereby for a 20min coating time, the LaPO_4 coated La revealed an apparent window of passivity over a potential range of $\sim 0.5\text{V}$. The anodic current densities realised for the 20min coating time were approximately 1.5 orders of magnitude lower than untreated La samples. The potentiodynamic polarisation curves in Fig 5 also illustrate that the dissolution characteristics of La are directly related to conversion treatment

time. However, most critically, the results clearly demonstrate that a LaPO_4 conversion coating can effectively reduce the rate of dissolution of La in aqueous media when conversion coated to form a sparingly soluble surface film.

3.4 Immersion testing of conversion coated bulk Lanthanum specimen

In order to provide a physical determination of the efficacy of LaPO_4 conversion coatings for pure La, the immersion response of both a bulk pure La specimen with and without a LaPO_4 conversion coating are seen in Fig. 6 (where the conversion coated specimen was conversion coated for 20min in 0.1M $\text{NH}_4\text{H}_2\text{PO}_4$ at 80°C).

The pure La specimen was freshly ground prior to immersion, in order to improve visualisation as pure La ingot will ultimately darken when left exposed in air. When immersed in 0.1M NaCl, untreated La exhibited numerous ‘pits-like’ regions of localised corrosion, following 1 minute, with corrosion having completely engulfed the La surface after ~10 minutes. For the pure La, it was also noted that for the whole period of immersion copious hydrogen bubbles were emanating from the surface. The corrosion products on the surface of the La do not induce a passivating response, however tend to promote further dissolution (phenomenologically similar to the case of pure Mg [23]). Conversely, the conversion coated La specimens exhibited minimal evidence of corrosion even after exposure for 30 minutes. It is noted that some bubbles (indicative of the cathodic reaction) were observed at the edges of the conversion-coated specimen, however these were ascribed to weak regions of the conversion coating at the specimen edges (and perhaps most like due to the presence of slight coating defects). None the less, in support of the electrochemical analysis, simple immersion testing was able to reveal that LaPO_4 conversion coating has the ability to effectively protect La from dissolution. The protective properties of the investigated LaPO_4 conversion coating on bulk La are promising.

3.5 Conversion coating upon lanthanum deposited AZ91D

Given that it has been demonstrated that the LaPO_4 conversion coating on bulk La restricts dissolution, and that the deposited La films upon on Mg-alloy AZ91D were able to serve as sacrificial, the next step is to combine these aspects to demonstrate a functional corrosion protection system for AZ91.

As such, the conversion coating demonstrated for pure La was produced upon the as magnetron sputtered La film upon AZ91D, and the corrosion evolution of the system was investigated. In order to provide a visual record of the performance, again, partially deposited La-films were generated using masking tape. The La-film was then immersed in 0.1M $\text{NH}_4\text{H}_2\text{PO}_4$ solution for 15 minutes (80°C) to induce the formation of LaPO_4 on the La film surface. An immersion time of 15 minutes was chosen to be a little more conservative with the rate of conversion from La film to LaPO_4 . Finally, the specimens were then immersed in 0.1 M NaCl solution and the in-situ corrosion behaviour monitored, as seen in Fig 7 (<https://www.dropbox.com/s/qzthyop39xkzr6z/Figure%207%20video.avi?dl=0>).

In the case of the non-conversion-coated La-film, it is noted that the La reacted immediately to sacrificially protect the AZ91D substrate (and this is more readily ascertained from the accompanying video). After ~40 minutes of immersion, corrosion sites were observed on the exposed AZ91D substrate, indicating that the majority of the sacrificial (uncoated) La film had lost its efficiency. In fact, small regions of the La film was also found to be non-existent, having been fully consumed.

Conversely, for the conversion coated La-filmed AZ91D specimens, they remained immune to dissolution for the same time period, i.e. up to 40 minutes. It is noted that a number of bubbles were observed at the specimen edges, however these were present for the entire test period and hence were not determined to be principally related to the corrosion behaviour.

Such results reveal that the corrosion resistance offered by the functional coating system upon AZ91D is indeed promising.

4. General discussion

Based on the idea of protecting Mg-alloys through coatings, a novel sacrificial anodic coating system was developed. This coating system not only revealed sacrificial protection ability, but equally as importantly it has an outer layer consisting of an insoluble conversion coating. The conversion coating had a minor influence on the electrochemical potential difference between the La film and the AZ91D Mg-alloy substrate. The results herein, whilst presenting performance over short time frames and in the laboratory setting, none the less demonstrate that even the very active engineering metal, Mg, can be adequately sacrificially protected. If such a coating system can be upscaled and proven to perform in industrial products, it will play an important role in improving and broadening the practical applications of Mg alloys. From a scientific perspective, more work is required on optimisation such as understanding the role of the La film thickness, the bond strength between the La film and Mg-alloy substrate, as well as optimising the conversion coating (i.e. altering coating bath temperature, solution concentration and the use of additives could be attempted in the future) – with a view to coating longevity.

Conclusions

Herein, we report a La coating upon Mg-alloy AZ91D, capable of serving as a functional anodic coating. The La-coating is capable of providing sacrificial corrosion protection to AZ91D. Such a form of ‘galvanising’ for Mg has not previously been demonstrated. Furthermore, it was demonstrated that a lanthanum phosphate (LaPO_4) conversion coating could be successfully achieved upon La coatings (and bulk La), and this LaPO_4 coating is insoluble and kinetically restricts La dissolution. The combination of a La-coating, and its subsequent conversion coating, results in a novel functional coating system for the active corrosion protection of AZ91D, whilst applicable more widely across a range of Mg-alloys.

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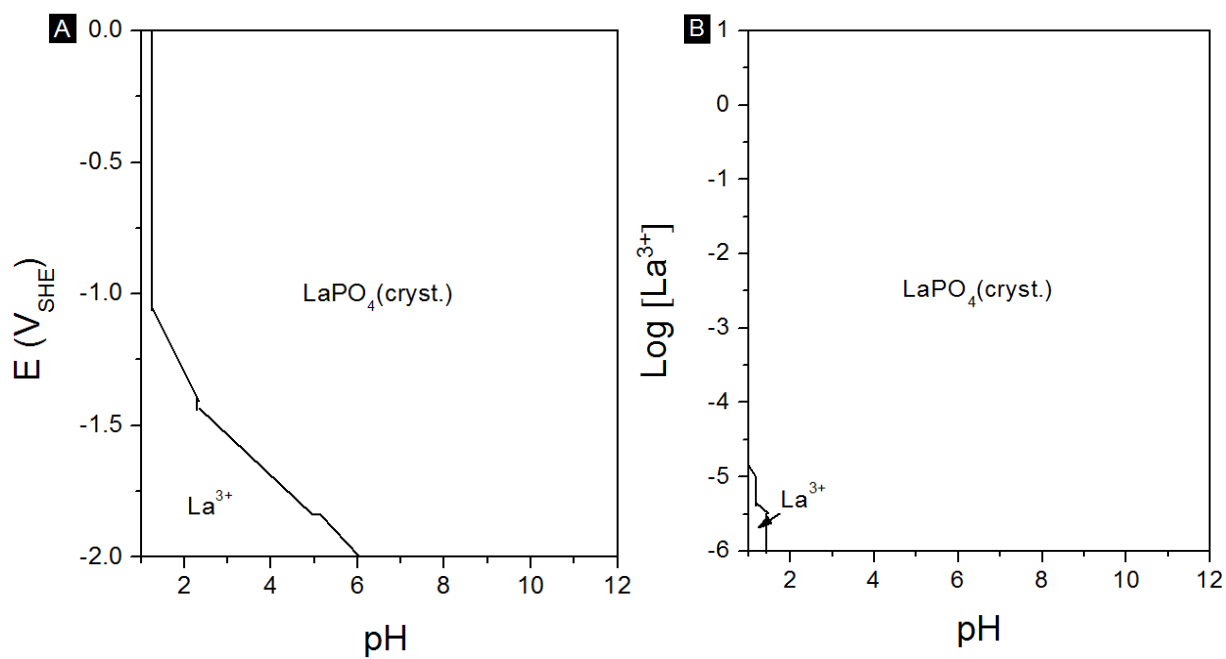


Figure 1. A) Predominance area diagram calculated for water with concentrations of 0.01M PO_4^{3-} and 1×10^{-5} M La^{3+} ; B) pH stability of LaPO_4 as a function of La^{3+} concentration (calculated with 0.01M PO_4^{3-} concentration at -1.7 V_{SHE}).

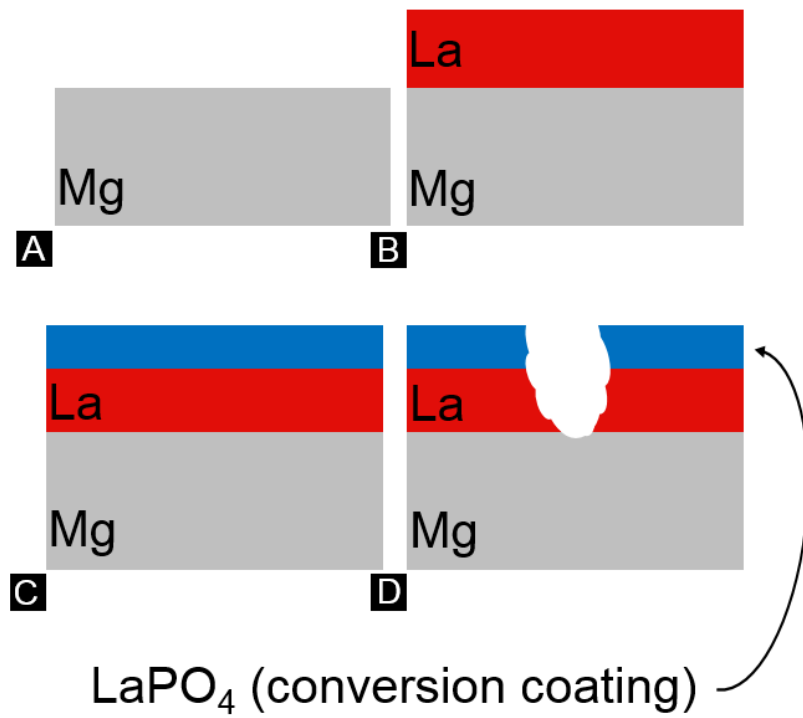


Figure 2. Demonstration of the formation and protection processes of our functional coating system. La was coated onto Mg substrate (from A to B); LaPO₄ was then formed on coated La surface (from B to C); La film will protect Mg substrate once the outer LaPO₄ conversion coating is damaged (D).

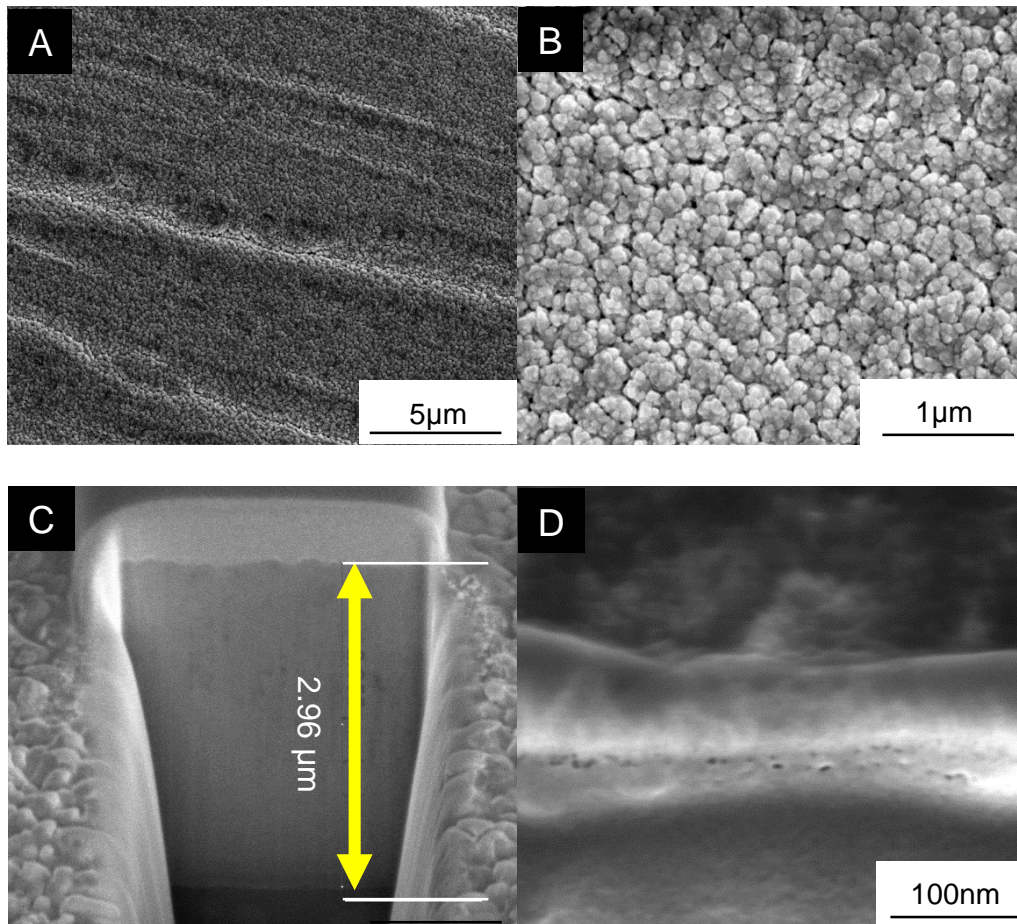


Figure 3. FIB SEM images of magnetron sputtered La film upon AZ91D after 2.5 hours sputtering with radio frequency power 200W. (A) and (B) indicate the surface morphology, (C) is a cross section image following ion milling, and (D) is La-AZ91D interface.

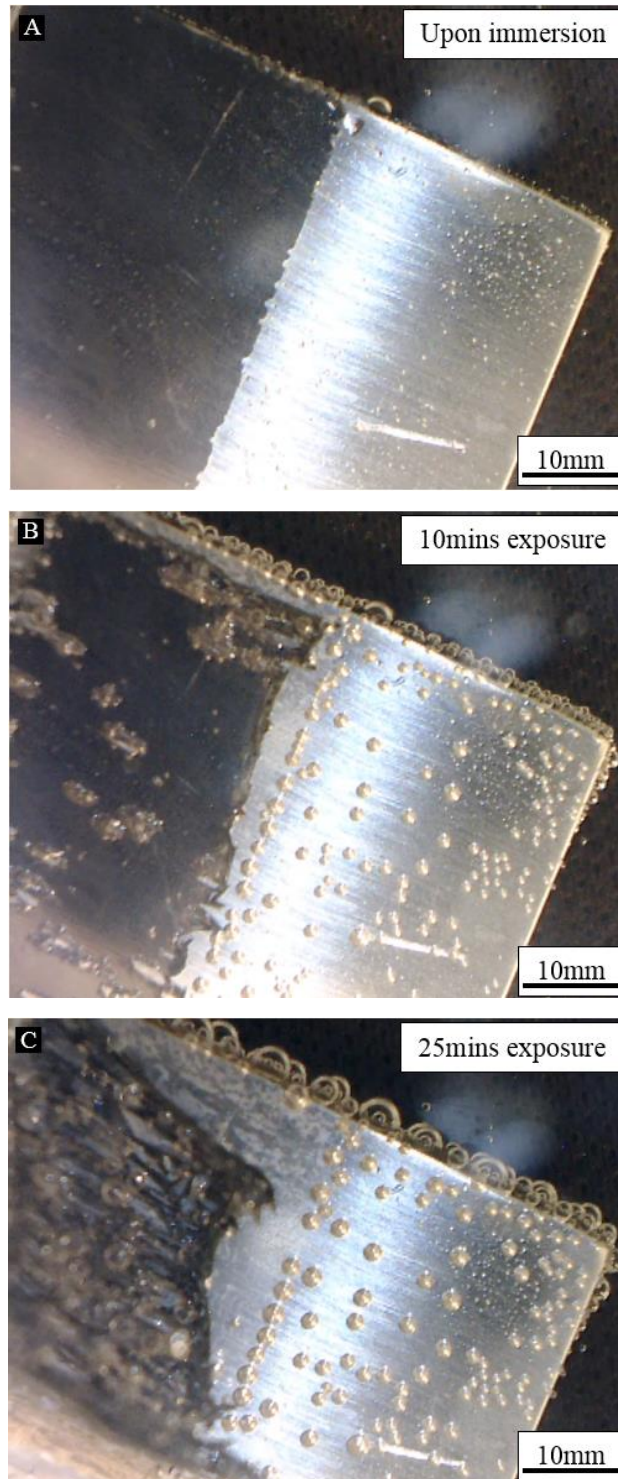


Figure 4. Photographs taken in situ during immersion of Mg AZ91D coated with anodic La film in 0.1M NaCl. (A) was taken upon immersion, (B) was taken after 10mins exposure to 0.1M NaCl solution and (C) was taken after 25mins exposure. Corresponding video at: <https://www.dropbox.com/s/d5l2cd27xz2zc73/Figure%204%20video.avi?dl=0>

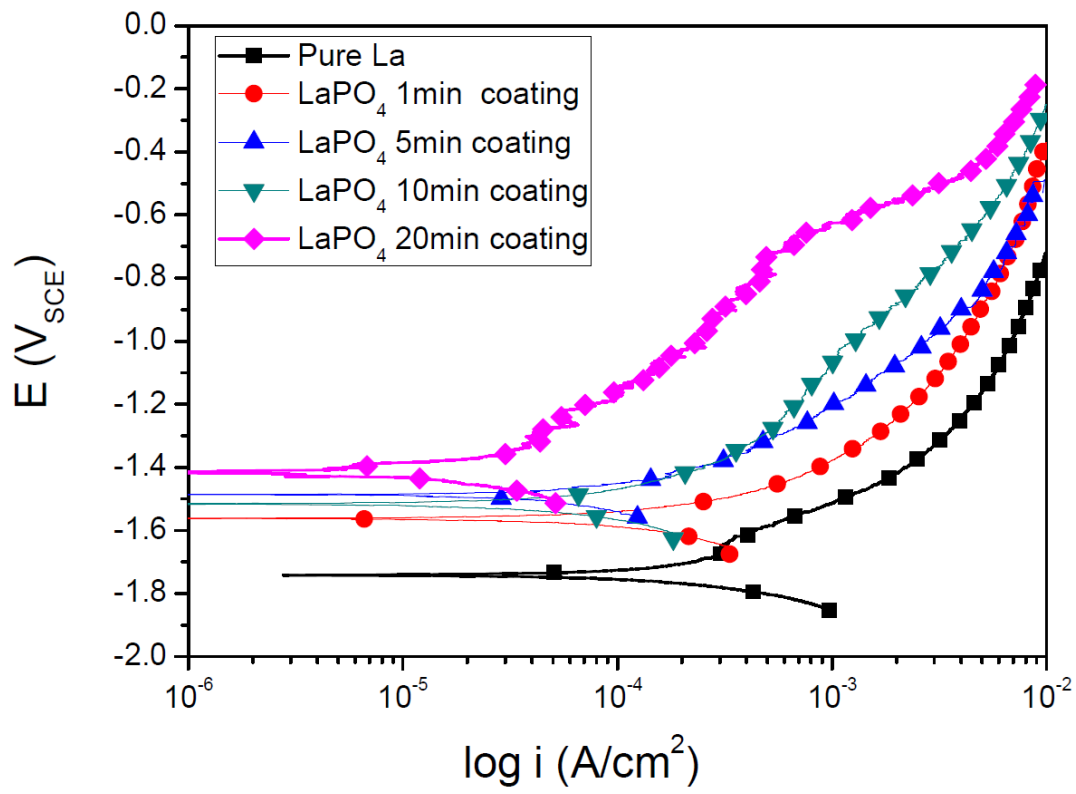


Figure 5. The potentiodynamic polarisation curve of lanthanum phosphate (LaPO₄) coated specimens with different treatment time measured in 0.1M NaCl solution.

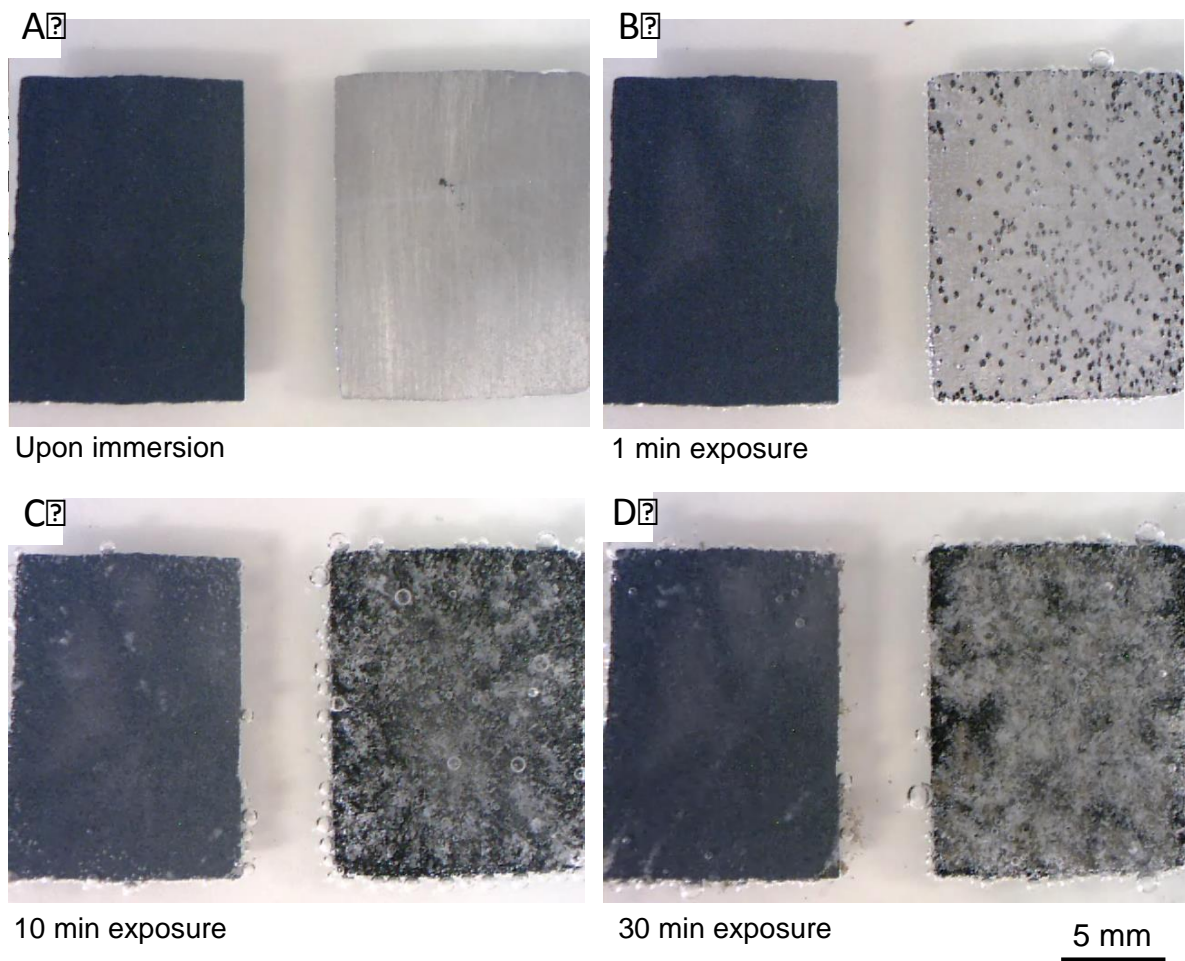


Figure 6. Immersion test for lanthanum phosphate (LaPO₄) coated specimens (left side of each image, treated by immersing La in 0.1 M NH₄H₂PO₄ for 20mins at a constant 80°C) and pure La piece in 0.1M NaCl solution. (A) was taken upon immersion, (B) was taken after 1mins exposure, (C) 10mins exposure and (D) 30mins exposure.

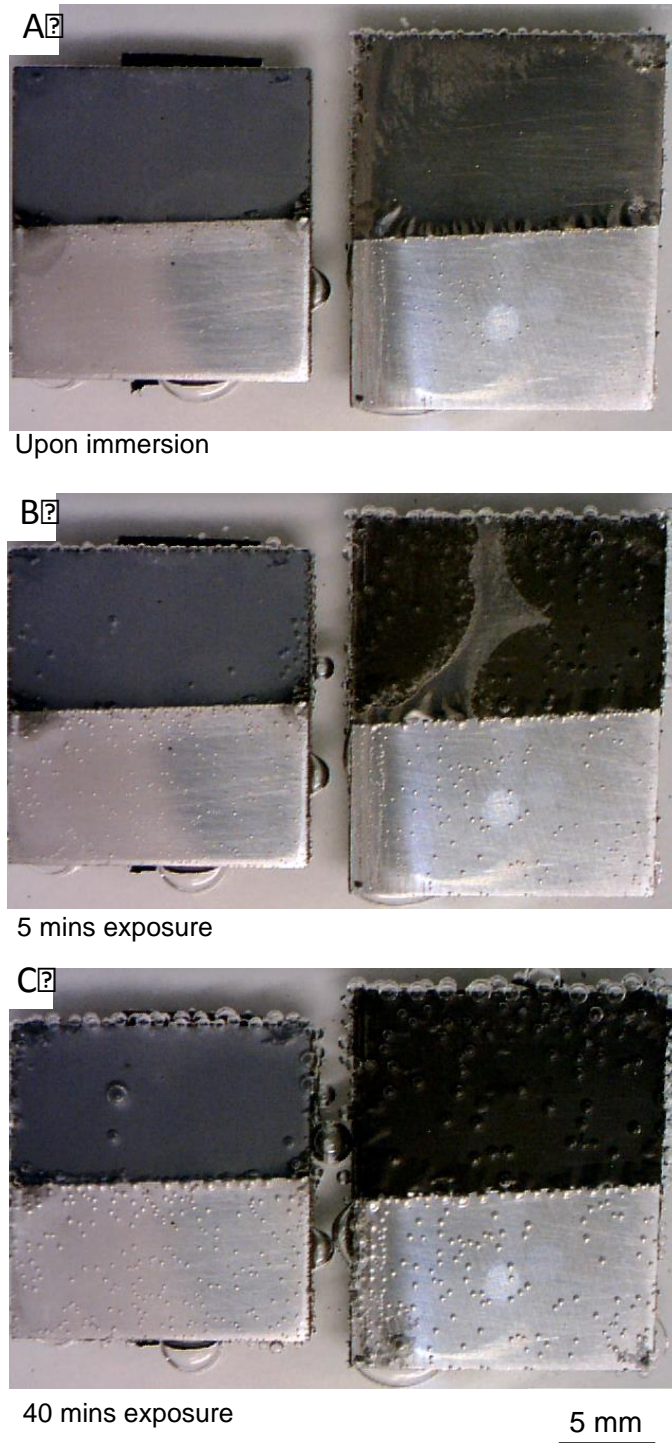


Figure 7. Photographs taken in situ during immersion of Mg AZ91D half coated with anodic La film (on the right hand side) and Mg AZ91D half coated with La and afterwards LaPO₄ coating in 0.1M NaCl. (A) was taken upon immersion, (B) was taken after 5mins exposure and (C) 40mins exposure.